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Polymer Electret Improves the Performance of the Oxygen-Doped Organic Field-Effect Transistors

Dongfan Li, Yuanwei Zhu, Peng Wei, Wanlong Lu, Shengtao Li, *Senior Member, IEEE*, Steven Wang, Ben Bin Xu, and Guanghao Lu

Abstract—Chemical doping is widely used in the electronic devices. In p-type semiconductor thin films, oxygen doping fills the hole traps and increases hole concentrations, improving the performance of the organic field-effect transistors (OFETs). Due to the low ionization potential for p-type semiconductors, the superfluous holes induced by the oxygen doping degrades the OFETs off-state leakage performance. On the other hand, for p-type semiconductors with high ionization potential (up to 5.5-6.0 eV), the limited oxidation of oxygen is hard to achieve satisfactory doping concentrations to fill the trap states. This refers to the well-known intrinsic incompatibility between the oxygen doping and high-performance OFETs. Herein, a novel strategy is introduced to overcome the incompatibility and achieve high-performance OFETs by using the structural polymer electret. That is, moderate hole concentrations induced by low-pressure (30 Pa) oxygen plasma fill the hole traps within semiconductor. And the built-in field resulted from polymer electret accumulates the holes inside semiconductor near the semiconductor/electret interface, thus improving the OFETs performance. Using a model organic semiconductor with high ionization potential-2,7-didodecyl[1]benzothieno[3,2-b][1]benzothiophene (C₁₂-BTBT) as an example, the high-performance OFETs with field-effect mobility (μ_{FET}) of 3.5 cm² V⁻¹ s⁻¹, subthreshold-swing (SS) of 110 mV decade⁻¹, on-off ratio of 10⁴, and widely-tunable threshold voltage (V_t) are realized at a low voltage below 2 V in the open air.

Index Terms—organic field-effect transistor, polymer electret, doping, organic semiconductor

I. INTRODUCTION

The organic field-effect transistors (OFETs) have attracted significant interests for its wide applications in next generation flexible electronics [1-3]. Oxygen doping, a common technique to process the p-type semiconductors, can be used to tune threshold voltage (V_t) by filling the trap states

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and increasing hole concentrations [4]. Since the ionization potential for p-type semiconductors is usually low, a higher hole concentrations is difficult to be depleted by gate voltage (V_{gs}), where the V_{gs} mainly modulates charge carriers near the interface between semiconductor layer and dielectric layer.

On the other hand, for p-type semiconductors with high ionization potential (up to 5.5-6.0 eV), the limited oxidation of oxygen makes it hard to achieve ideal doping concentration to fill the trap states, which has been known as the intrinsic incompatibility between the oxygen doping and high-performance OFETs [5-6].

These challenges significantly limit the applications of oxygen doping in the modern development of high-performance OFETs. In fact, the community of organic electronics has been forced to seek alternative organic [7-8] or inorganic [9] dopants, which are normally more expensive than oxygen. The quest of developing the low-cost oxygen as an effective dopant towards high-performance OFETs technology remains ongoing.

With this regard, we propose a combined strategy using the oxygen doping and polymer electret to achieve the high-performance OFETs, based on a model semiconductor with high ionization potential-2,7-didodecyl[1]benzothieno[3,2-b][1]benzothiophene (C₁₂-BTBT) [10-14]

II. EXPERIMENTAL

A. Materials and Device Fabrication

Polystyrene (PS, $M_w = 2000$ kDa, PDI = 1.3) was purchased from Sigma-Aldrich and used as received. PS was dissolved in o-dichlorobenzene with a concentration of 5 mg ml⁻¹, which was then spin-coated on the clean Si/SiO₂ substrate. The thickness of PS varied from 0-21 nm, which can be achieved by controlling the spinning speed. Then the PS coated substrate is annealed in the open air at 120 °C for 30 min to dissipate residual solvent. Subsequently, a nominal 40 nm C₁₂-BTBT film was thermally evaporated onto the substrates in the vacuum chamber ($< 10^{-4}$ Pa, 0.1 Å s⁻¹). C₁₂-BTBT was synthesized via an in-house experiment.

The gold source and drain electrodes (40 nm) were deposited using a shadow mask ($< 10^{-4}$ Pa, 0.5 Å s⁻¹) with a channel length (L) of 300 μm and a channel width (W) of 3000 μm. The total capacity (C_{total}) per unit area of 10 nm PS coated 300 nm SiO₂ is 10.94 nF cm⁻², calculated by $1/C_{\text{total}} = (1/C_{\text{SiO}_2} + 1/C_{\text{PS}})$, $C_{\text{SiO}_2} = 11.5$ nF cm⁻², $C_{\text{PS}} = \epsilon_0 \cdot \epsilon_{\text{PS}}/d$, and $\epsilon_{\text{PS}} = 2.55$ [15].

B. OFETs Characterization

The OFET characteristics were performed using an Agilent Keysight B2900A Quick I - V measurement system in the ambient condition. Before measurement, we gently scrape the

surface of C₁₂-BTBT film to separate the OFETs on the same substrate to reduce the parasitic current paths.

C. Oxygen Plasma Treatment

The oxygen plasma treatment was applied to the OFETs using FEMTO from Electronic Diener Plasma-Surface-Technology (13.56 MHz).

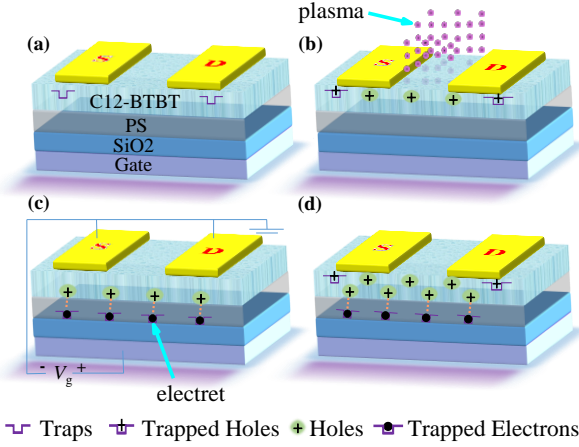


Fig. 1. The schematic diagram of C₁₂-BTBT/PS-based OFETs using oxygen plasma in combination with gate-stress. (a) Device configuration. (b) The charge traps are filled by plasma-induced doping. (c) Manipulating the hole concentrations inside C₁₂-BTBT film by adding polymer electret. (d) A combined strategy using the oxygen doping and polymer electret to improve the OFETs performance by tuning the hole concentrations throughout the whole C₁₂-BTBT film.

III. RESULTS AND DISCUSSIONS

The OFET is fabricated in a typical layer by layer structure of bottom gate | SiO₂ | PS | C₁₂-BTBT | source and drain electrodes (Fig. 1). Low-pressure (30 Pa) plasma initiates the oxygen doping upon C₁₂-BTBT [10], thus V_t can be tuned. PS, soluble as well as low cost, is featured into a quality thin film to be used to trap the electrons. Once the electrons injected from the source and drain electrodes is trapped, these electrons can be stored in PS for a relatively long time [15], which is the so-called polymer electret. The electret provides a built-in field to accumulate the holes within C₁₂-BTBT, which increases hole concentrations and further improves the OFETs performance. It is worth noting that the polymer electret can also be achieved by applying V_{gs} for a few minutes while keeping the source and the drain electrodes grounded [16].

Apart from acting as a polymer electret, PS layer also plays another role as a passivation layer to shield the charge traps on the surface of SiO₂ [17]. Due to the intrinsic charge traps of SiO₂, C₁₂-BTBT-based OFETs using the naked SiO₂ presents a poor performance (Fig. 2a).

The thickness effect of PS on μ_{FET} and onset voltage shift (ΔV_{on}) are investigated. ΔV_{on} is defined as the onset voltage discrepancy between the as-prepared OFETs and OFETs treated by +90 V stress (Fig. 2a). By varying the PS thickness from 0 to 21 nm, we find that both μ_{FET} and ΔV_{on} achieve the maximum values when the thickness of PS is 10 nm. Therefore, 10 nm PS was used in this work (Fig. 2b).

While it is widely acknowledged that the thick PS film can reduce the capacitance and thus deteriorates the low-voltage performance, the thin PS film is also unfavorable for a low-voltage operation. The electrons are originally injected from

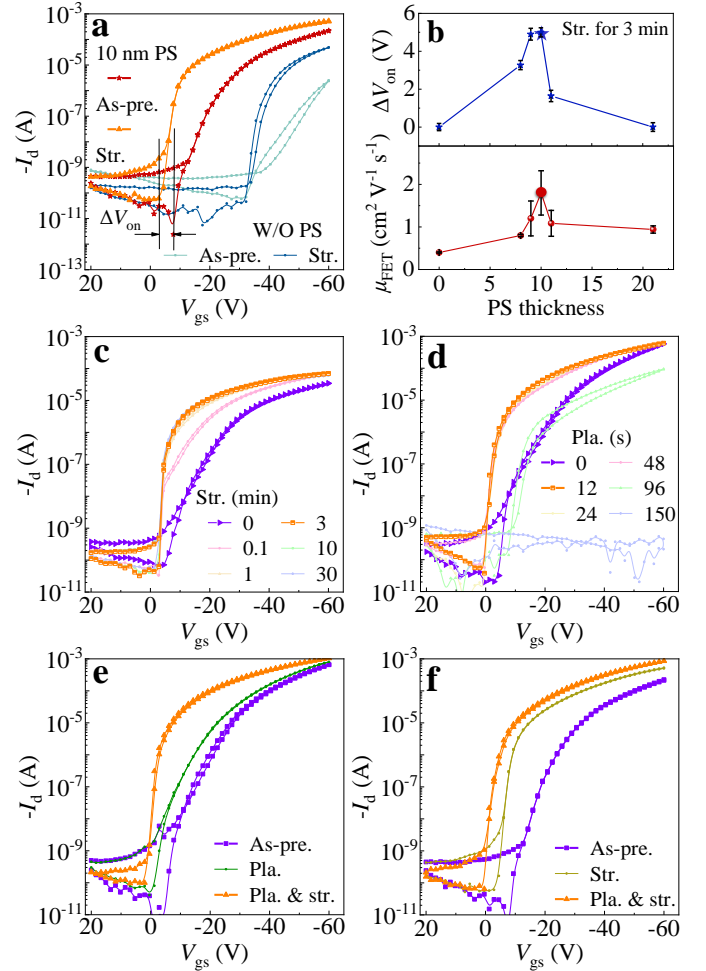


Fig. 2. PS electret improves the OFETs performance. (a) The transfer curves with and without a PS layer. “W/O PS” denotes the OFETs without PS. “As-pre.” denotes the as-prepared OFETs without gate stress or plasma treatment. “Str.” denotes a +90 V stress treatment. (b) The plot of μ_{FET} and ΔV_{on} vs. PS thickness. (c) In-situ transfer curves after +90 V stress treatment for different stress time. (d) In-situ transfer curves after oxygen plasma treatment for different treatment time. “Pla.” denotes a low-pressure (30 Pa) oxygen plasma treatment. (e-f) Tuning V_t of the C₁₂-BTBT/PS-based OFETs by plasma and/or +90 V stress treatment. Note that V_{ds} is set as -60 V.

the source and the drain electrodes into the C₁₂-BTBT, then the electrons accumulated in the C₁₂-BTBT were transferred to the PS layer. Compared with PS, C₁₂-BTBT possess the advantage with a deeper LUMO level. Therefore, the transfer of electrons accumulated inside the C₁₂-BTBT into PS requires extra energy (e.g. electric field) to overcome this barrier. The critical V_{gs} for the accumulation of electrons inside PS layer is given as follow [16]:

$$e | V_{gs} | = \frac{|E_{C12-BTBT} - E_{PS}|}{d_{PS}} (d_{SiO2} \frac{\epsilon_{PS}}{\epsilon_{SiO2}} + d_{PS})$$

where e is the element charge; E is the LUMO level; ϵ is the permittivity and d is the thickness.

We investigate the dependence of drain current (I_d) on stress time (from 0 s to 30 min), and find that I_d no longer increases after applying the gate-stress (+90 V) for 3 min (Fig. 2c). The gate-stress induced hysteresis can be eliminated soon as completing V_{gs} scanning twice [18-19]. While a higher V_{gs} is likely to cause a larger ΔV_{on} , it could also damage the OFETs.

After oxygen doping, I_d no longer increases after a plasma treatment for 12 s (Fig. 2d), and extended duration (> 48 s) leads to a degradation on I_d due to the removal of semiconductor molecules by plasma etching [20]. The etching rate can be controlled by manipulating the chamber pressure and 150 s is considered to be the total time to remove 40 nm C_{12} -BTBT film. An etching rate of oxygen plasma (30 Pa) upon the evaporated C_{12} -BTBT film is then concluded as ~ 0.26 nm s^{-1} . Based on above, a gate-stress (+90 V) of 3 min with a plasma treatment time of 12 s are synergistically used in this work, to enable a widely-tunable V_i without decreasing on-off ratio (Fig. 2e-f).

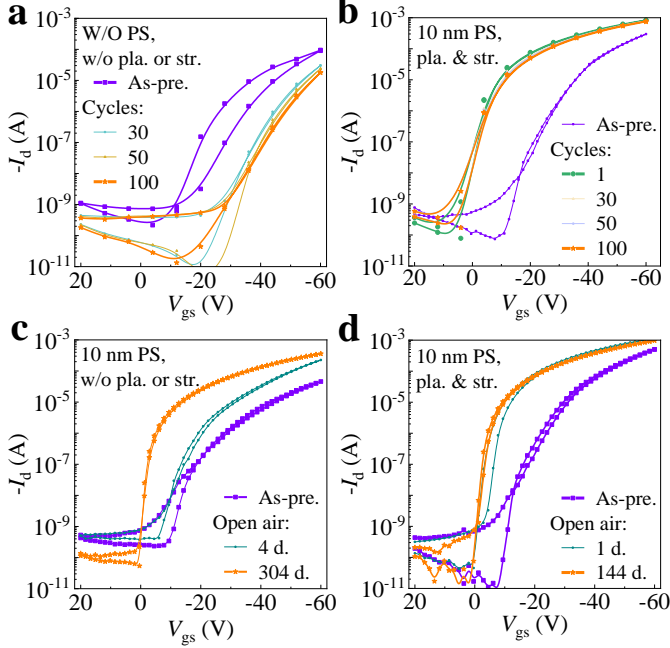


Fig. 3. The stability test for OFETs. Operational stability after 100 cycles: (a) without plasma or gate-stress treatment, and (b) with plasma & gate-stress treatments. The abbreviation of “w/o pla. or str.” denotes the as-prepared OFETs without plasma or gate-stress treatment. Environmental stability over 100 days in the open air: (c) without plasma or gate-stress treatment, and (d) with plasma & gate-stress treatments. The abbreviation of “d.” denotes the OFETs were placed in the open air for days. Note that V_{ds} is set as -60 V.

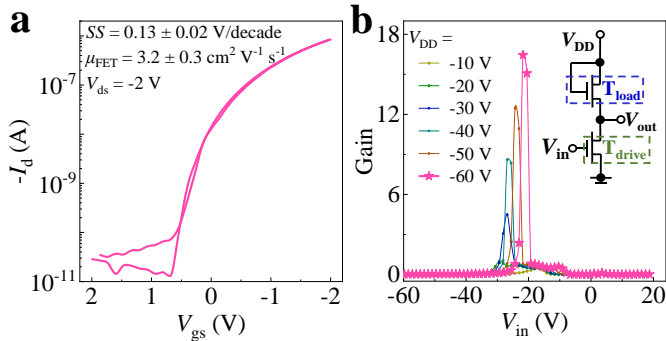


Fig. 4. The applications for circuits using the OFETs with an oxygen-doped C_{12} -BTBT/polymer electret configuration. (a) The transfer curves of the C_{12} -BTBT-based OFETs with a 10 nm PS layer coated on 300 nm SiO_2 . The statistic of SS and μ_{FET} were obtained from over 20 OFETs with a channel length of 300 μm . (b) The gains of an inverter at different operation voltages. T_{drive} and T_{load} denote the OFETs were treated with and without plasma & gate-stress treatments, respectively.

As a well-known fact that molecular dopants can improve the OFETs stability by filling the trap states [21-24], we next study the operational and environmental stability (Fig. 3), which are

the key factors for assessing the characteristic of OFETs. The OFETs without PS show a poor operational stability (Fig. 3a), however, the OFETs with 10 nm PS layer present significant improvement in the operational stability due to the shield of charge traps on the bare SiO_2 (Fig. 3b). Moreover, the OFETs with a 10 nm PS layer show a good environmental stability for over 100 days (Fig. 3c), and plasma & gate-stress treatments cast limited effect on the stability (Fig. 3d).

Based on the above strategy, OFETs using 300 nm SiO_2 can work well at a low voltage (2 V) with μ_{FET} of 3.5 $cm^2 V^{-1} s^{-1}$, SS of 110 mV decade $^{-1}$ and on-off ratio of $\sim 10^4$ (Fig. 4a). The reactive oxygen doping facilitated under a low-pressure plasma treatment, which is used to tune V_i towards 0 V, has been proven as an essential for a low voltage operation. And an additional electric field, induced by polymer electret, also contributes to this low voltage operation. Moreover, a digital inverter with a high gain of 16 (Fig. 4b) has been successfully fabricated and demonstrated.

IV. CONCLUSION

In this work, a combined strategy using the oxygen doping and polymer electret is described to regulate charge transport in the OFETs. With this approach, the organic semiconductor with high ionization potential (e.g. C_{12} -BTBT) shows an excellent performance, even without those expensive synthetic organic or inorganic dopants.

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